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PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

A method for improving the Properties of Cellulosic Textile Materials

We, LIPACO S.A., a Corporation organised under the laws of the Canton of Basle, Switzerland, of Elisabethenstrasse 8, Basle, Switzerland, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new textile process and in particular to a new process for imparting wash-wear properties to cellulosic textiles.

With the installation of automatic washing and drying machines in many households, there has been a great demand for so-called wash-wear garments. Broadly speaking, wash-wear garments are those which, after washing and drying by conventional methods, recover or retain an ironed appearance without pressing. An index to the wash-wear properties of a given fabric are its wet and dry crease recovery angles. The procedure for determining the dry crease recovery angle is given in Test D1295—53T of the American Society for Testing and Materials. Wet recovery angle is determined in the same way except that the fabric is first saturated with water.

Various processes have been proposed for imparting suitable crease recovery properties to cellulosic textile materials. The majority of such processes involve the use of resinous materials which are capable of cross-linking the cellulose chains. In applying these agents the normal practice is to impregnate the textile material with an aqueous resinous solution, dry the material and then bake it at an elevated temperature to effect reaction between the resin and the cellulose.

It is also known to react cellulose fabrics with various non-resinous modifying agents such as epichlorohydrin or a dichloropropanol. These materials are normally applied to the

fabric in the presence of alkali while the fabric is wet and highly swollen. A conventional technique is to apply the reagent and the alkali to the fabric, wind it on a roller and then store it, wet, in an air-tight container, for up to 12 hours. Reaction occurs during storage. Such processes have advantages over resin treatments. Their products are much more fast to washing and are not subject to the chlorine retention and yellowing which are experienced with many resin treatments.

Comparison of the products of all of these processes, however, indicates that much is left to be desired in producing a textile having true wash-wear properties. Thus, when the cross-linking reaction is carried out on dried material, as is normally the case with resin treatments, the crease recovery properties of dry fabric are good but if it is attempted to put sufficient resin into the fabric to give good wet crease recovery properties, the physical properties, particularly tensile strength, are adversely affected. In practical terms, what this means is that while resin-treated garments can be washed and "drip-dried" to give a satisfactory ironed appearance, if they are tumble dried, as in a conventional home drier, they do not have an iron appearance.

When, on the other hand, wet treatments are applied, the wet crease recovery of the garments is good, but if they are rumpled in the dry state they do not easily recover.

It has been attempted to get the best of both worlds by combining a conventional resin treatment with a wet treatment, e.g. a treatment with epichlorohydrin. However, this is at best doubtful compromise. The defects of the resin treatments such as low wash fastness, yellowing and chlorine retention are carried over into the combined process. Often the resin is lost in substantial

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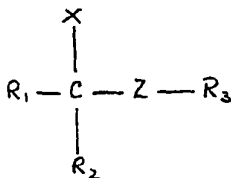
measure in the wet treatment itself. Moreover, with some resins, the wet reagent, e.g. epichlorohydrin, tends to combine with the resin rather than the cellulose and is consequently lost with the resin in subsequent washings.

It is an object of the present invention to provide an integrated process whereby improved crease recovery properties, both wet and dry, may be obtained.

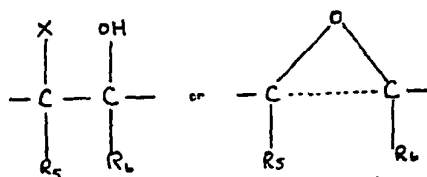
In accordance with the invention, this and other objects are achieved by means of a process which comprises cross-linking a cellulosic textile material with formaldehyde while the material is substantially dry as hereinafter defined, and reacting the cellulosic material with a chain bulking agent, as hereinafter defined, while said material is in a swollen state, either before or after cross-linking.

The term "chain bulking agent" is used to describe a class of materials which are capable of reacting with the cellulose to give a molecule which is substantially bulkier than the initial cellulose chain. The chain bulking reagents used should be organic compounds having at least three carbon atoms in the molecular chains or being capable of forming chains of that length under the reaction conditions and containing at least one group capable of reacting with cellulose. Cross-linking agents are, of course, a species of chain bulking agents. However, chain bulking need not involve cross-linking. Thus high wet crease recovery has been obtained with monofunctional reagents. Since the reagent is monofunctional, cross-linking cannot take place. However, by the reaction, the cellulose chains are made bulkier and more tightly packed. Relative movement of the chains becomes more difficult. Hence the textile tends to return to the physical configuration in which the reaction was conducted, resulting in good wet crease recovery properties.

The chain-bulking agents which are preferably used in the process of the present invention have formulae of the following

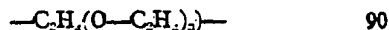


where X is halogen, preferably chlorine or bromine, R_4 is a divalent connecting radical; Z is either

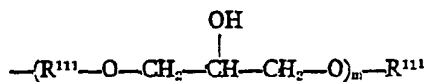


and R_1 , R_2 , R_3 , R_5 and R_6 are hydrogen or radicals which are less reactive to cellulose than the halohydrin or epoxy groups. Under the conditions conventionally employed, the groups R_1 , R_2 , R_3 , R_5 and R_6 are substantially unreactive to cellulose.

R_1 , R_2 , R_3 , R_5 and R_6 in the above formulae in each instance preferably represent hydrogen since such compounds are the most readily prepared but they can in one or more instances represent lower alkyl groups such as methyl or ethyl, hydroxyalkyl groups such as hydroxymethyl or hydroxyethyl monocyclic aryl groups such as phenyl or tolyl, cycloalkyl groups such as cyclohexyl, haloalkyl groups such as chloromethyl and chloroethyl, or R_1 and R_3 can together represent a divalent connecting radical such as a methylene or an ethylene radical. The only requirement is that R_1 , R_2 , R_3 , R_5 and R_6 must not be such as to prevent the compound from reacting with the hydroxy group of a cellulose molecule. R_4 can represent any divalent connecting group such as methylene, ethylene or propylene; a hydroxyalkylene group such as hydroxypropylene; or a group of the formula $-\text{R}-\text{Y}-\text{R}^1-\text{Y}-\text{R}^{11}-$ wherein Y represents oxygen or sulphur; R and R^{11} represent lower alkylene groups such as methylene or ethylene; and R^1 represents any divalent connecting radical as illustrated by a lower alkylene group; a lower hydroxyalkylene group such as 2-hydroxypropylene; a monocyclic aryl radical such as phenyl or tolyl; a radical of the formula



wherein n is an integer of from 1 to 20; or a radical of the formula



wherein m represents an integer of from 1 to 5 and R^{11} represents a divalent hydrocarbon radical as illustrated by



Compounds of the latter type result when

epichlorohydrin is reacted with less than an equimolar quantity of a dihydric alcohol or phenol. It should also be mentioned that when a compound corresponding to one of the formulae in the preceding paragraph contains two Z groups, the groups may be the same or different. Specific illustrative examples of suitable chain bulking compounds are: epichlorohydrin, 1,3-dichloro-2-propanol, 2,3-dibromo-1-propanol, m-di(β , γ -epoxypropoxy) benzene, 1,3-di(β -hydroxy- γ -chloropropoxy)-2-propanol, 1,2-di(β -hydroxy- γ -chloropropoxy)-ethane, 1,2-di(β , γ -epoxypropoxy) ethane, 1,2; 3,4-diepoxybutane, 1,2; 5,6-diepoxyhexane, 1,5-dihydroxy-2,4-dichloro-cyclohexane and 2,6-dichloro-3,4,5-trihydroxy-5-hydroxymethylheptane. Of these epichlorohydrin is preferred.

The use of such compounds in rendering cellulosic fabric dimensionally stable is known per se and is disclosed, for example, in Patent Specification No. 855,547.

Although it may be applied to raw fibre, yarns and thread, the invention has its greatest usefulness as applied to cellulosic fabrics. Such fabrics may be of woven or knitted construction or fabrics or other kinds, for example the so-called non-woven fabrics. The fabric may consist wholly of cellulose fibres or in part of these fibres and in part of fibres or other kinds, for example, cellulose acetate (acetone-soluble cellulose acetate or cellulose triacetate), or fibres of synthetic linear polymers, for example of polyamides such as nylon 6 or nylon 66, or of polyesters, for example polyethylene terephthalate, or of addition polymers derived from acrylonitrile.

The cellulose fibres may be of natural origin such as cotton, linen, hemp, jute, ramie or sisal or of synthetic origin, i.e. rayon made by the viscose, cuprammonium or nitrate process or by the saponification of organic esters of cellulose, e.g. cellulose acetate.

In the fabric the fibres may be used in the form of staple fibre or continuous filament. When blended fabrics are treated, they preferably contain at least 35% of cellulose by weight.

In carrying out the present process, the cellulosic textile material is preferably first-cross-linked with formaldehyde. While it is within the scope of the invention as broadly conceived to employ any technique for conducting the cellulose-formaldehyde reaction, preferably the reaction is carried out in accordance with the teachings of our Patent Specifications Nos. 930,132 and 936,761.

These applications teach the reacting of cellulose with formaldehyde by impregnating the cellulose with formaldehyde, water and a catalyst which is zinc sulphate or a salt of a bivalent group II metal with a monobasic acid which is ionised to the extent of at least 50% when in normal aqueous solution at

18°C. and then drying and heating the impregnated cellulose.

The catalyst should preferably be soluble and form no precipitate in aqueous solution at pH 5 at concentrations of at least 0.03 mols/litre at 20°C. For reasons explained more fully below, solutions at pH 6 or above are highly desirable for cotton and, therefore, when cotton is to be treated, the catalyst should be soluble at that pH. Salts which remain soluble at higher pH are, of course, more advantageous. Obviously, salts which are highly coloured or highly toxic or become so during the process are undesirable.

Salts which meet these qualifications are in general those in which the metal is bivalent and belongs to Group II of the periodic table and the acid radical is that of a monobasic acid which is at least 50 *per cent* ionised in normal aqueous solution at 18°C., such as hydrochloric, hydrobromic, hydriodic, nitric, perchloric and thiocyanic acids. Of most interest are salts of calcium, magnesium, strontium, barium and zinc. Examples of suitable salts would include calcium chloride, bromide, iodide, nitrate and thiocyanate, magnesium nitrate, chloride, bromide, perchlorate and iodide, zinc chloride and nitrate and the chlorides of strontium, barium and cadmium. Zinc sulphate may also be employed. Either the anhydrous salt or a hydrate may be used, as may mixtures of salts. Generally the magnesium salts are preferred as being less acidic (in the classical sense) than the zinc salts and more effective (as curing agents) than the other salts mentioned. The magnesium halides are especially favoured and of these magnesium chloride is outstanding.

Magnesium chloride is of exceptional value in the present process for several reasons. Firstly, it is stable in solutions with formaldehyde at pH values up to about 9. This enables even the most sensitive cellulose material to be impregnated and dried with minimal damage. Moreover, magnesium chloride has a very pronounced effect in lowering the vapour pressure of formaldehyde, possibly as the result of complex formation. This tends to prevent loss of formaldehyde during curing, increasing the efficiency of the process.

The formaldehyde may be derived from any convenient source. Normally the commercial 40% solution is employed. Other sources, e.g. paraformaldehyde may, however, be employed as desired.

The formaldehyde and catalyst are normally applied from aqueous solutions. Other solvents, e.g. methanol and/or ethanol, may be present without detrimental effect but the solution should contain at least 10% by weight of water. Separate solutions may be used for the formaldehyde and catalyst but no advantage is gained thereby.

The concentration of formaldehyde may vary to a considerable extent depending on whether natural or regenerated cellulose is treated and on the fabric construction.

5 In general, it has been found that the amount of catalyst deposited on the fibre and the efficiency of the catalyst in reacting unbound formaldehyde with cellulose are more significant than the concentration of
10 formaldehyde in the solution, provided that enough formaldehyde is present during curing to furnish the quantity of formaldehyde required to be bound to the cellulose for the particular physical properties sought. An
15 overall range of recommended concentrations would extend from 0.5% to 6% by weight. Viscose rayon fabric will normally require 1 to 6%; cotton fabric 0.5—4.0% by weight. It will be understood that higher concentrations
20 may be employed, but serve no useful purpose. Indeed, it is one of the advantages of the use of the above catalysts that relatively dilute formaldehyde solutions can be used. Such solutions are less apt to lose
25 formaldehyde by evaporation and are easier to work with from the point of view of the health and comfort of the operator than the more concentrated solutions prescribed in many other processes.

30 The concentration of catalyst may vary considerably, depending on the catalyst. Normally it will be between 0.03 and 0.90 g.-mols./litre; preferably between 0.1 and 0.45 g.-mols./litre. However, it is the proportion
35 of catalyst deposited on the fibre and, to the extent that the minimum amount of formaldehyde must be present during curing, the molar ratio of catalyst to formaldehyde, which is significant.

40 The pH of the solution will depend on the material being treated. Natural cellulose, such as cotton, is generally more sensitive to acid degradation and therefore, when cotton is to be treated, a higher pH must be used than
45 is necessary with regenerated cellulose. Generally the treating solution pH should not be less than 5 for regenerated cellulose and not less than 6 for cotton.

50 Some of the salts listed above when put into water with formaldehyde at use concentrations will not give pH's in this range. When used in the present invention they are, therefore, preferably buffered, for example
55 with sodium carbonate, sodium bicarbonate or sodium hydroxide, to a pH of at least 5, or at least 6 if cotton is to be treated.

60 While the upper pH limit is not especially critical, some of the salts most useful with the present invention will form precipitates at pH's above 10.

The temperature of the treating solution is not especially significant. Room temperature is satisfactory, although lower temperatures may be used to prevent loss of
65 formaldehyde. Normally, temperatures of the

order of 15°C. to 50°C. are used.

The treating solution is applied to the cellulose material in such a manner that after impregnation (and drying) the material contains at least 0.003, normally between 0.0038
70 and 0.09 g.-mols, and preferably between 0.008 and 0.054 g.-mols, of catalyst per 100 g. of cellulose. Sufficient formaldehyde is picked up so that, bearing in mind losses in drying and curing, between 0.1% and 3%,
75 will remain on the fibre after curing. For reasons of economy the molar ratio of catalyst to formaldehyde deposited on the fibre or fabric is usually at least 1:17, normally from 1:17 to 5:1, and preferably from 1:12 to
80 1:1.

In applying the treating solution or solutions to fabric, any of the techniques well known to those skilled in the art may be used. Normally the solution is padded on to the
85 fabric; however, any other conventional technique, e.g. sprays, may be used as desired. In any case the treatment is preferably carried out so that, after removal of excess liquor by squeezing or other means, between
90 120 and 80% of liquor (based on the weight of bone dry unimpregnated material) remains on the material.

Following impregnation, the material is made substantially dry, i.e. its moisture content is reduced to not more than 2% by
95 weight of bone dry cellulose, and normally to less than 1%. This may be done by heating at say 30°—110°C. for whatever time is required to reduce the moisture content to the required amount. Following drying the material may be cured by heating to temperatures from 110°C. to 180°C. for periods
100 which may range from say 30 minutes to a few (say 5) seconds.

105 The temperatures and time for curing must be selected, having in mind the pH at which the treatment has been conducted and the curing agent used. Thus, where a pH of 5 has been used, curing must be conducted
110 under mild conditions within the range set forth; i.e. if a high temperature is used, a very short time should be used, or if a long time is used, the temperature should be low, within the range set forth. If more rigorous
115 curing conditions are employed and the impregnation was at a low pH, there is a danger of tendering the material.

By their nature most of the catalysts are capable of forming hydrates and, since the present treatment involves application of
120 aqueous solutions, the catalyst is normally deposited as a hydrate. With most salts, at least a part of the hydrate water is evolved during curing. It has been found that during
125 this water evolution the cellulose-formaldehyde reaction is inhibited or at least markedly depressed. To avoid such inhibition or depression it is therefore desirable to conduct the curing at temperatures either above,
130

below or between the range or ranges at which the particular catalyst used loses large amounts of water of hydration.

5 Since it is desirable to conduct curing as expeditiously as possible, temperatures below dehydration temperature are not usually employed. At the same time extremely high temperatures are to be avoided for fear of damage to the cellulose.

10 Because of these factors, salts which can be heated at intermediate temperatures without water evolution are extremely desirable as catalysts, other things being equal. One of the properties that makes magnesium chloride especially attractive as a catalyst in the present process is that although it loses some water at about 120°C., there is an intermediate temperature range in which comparatively little water is evolved and the compound can therefore function effectively as a catalyst without a prolonged curing time or an excessively high temperature.

Zinc salts are generally more likely to cause degradation than, say, magnesium salts and greater care must be exercised in curing when the catalyst is a zinc compound.

As the pH of the treatment is increased, more rigorous curing conditions may be used, within the range set forth, without adversely affecting the properties of the material.

30 Obviously the drying and curing steps may be obtained in a single treatment, if desired.

Following the curing stage, the cellulose may be washed, if desired, with ammonia, urea or other formaldehyde acceptors to remove unbound formaldehyde and catalyst.

At this stage of its processing the fabric contains between 0.10 and 3.0%, by weight of formaldehyde chemically bound directly to the cellulose (based on the weight of air dry unimpregnated cellulose) as determined by the amount of formaldehyde liberated by complete hydrolysis of the cellulose with 12N H₂SO₄. The formaldehyde is considered to be present as methylene or methoxy (—OCH₂—) chains cross-linking the cellulose molecules together. The fabric has a much reduced water inhibition and its tendency to swell in dilute caustic alkali is also greatly reduced. In the case of regenerated cellulose fabric it is no longer soluble in cuprammonium hydroxide. It is dimensionally stable.

The crease recovery properties of the fabric at this stage are also improved. Dry crease recovery is from 50° to 150° (the sum of warpwise and weftwise measurements) higher than untreated fabric. Wet crease recovery is usually also improved but to a lesser extent, say 50° to 100° higher than untreated fabric.

In accordance with the preferred sequence of steps, the fabric after having been cross-linked with formaldehyde is then reacted with a chain bulking agent, while the cellulose

fibres which it contains are in a highly swollen state. Advantageously this last stage is performed in the presence of an alkaline catalyst.

The amount of water necessary to swell the cellulose in terms of the present process is a rather elastic quantity. Rationally it should be at least the maximum amount of water which the fabric can be expected to pick up in a typical washing. Empirically it is found that good results are obtained if the fabric contains between 80 and 120% water, based on bone dry cellulose.

The alkaline catalyst may be any of the common bases such as the alkali metal hydroxides, for example sodium or potassium hydroxide, or salts of strong bases and weak acids, for example sodium sulphide or sodium silicate. Organic bases, such as quaternary ammonium compounds, for example trimethyl ammonium hydroxide, may also be employed. Potassium hydroxide is the preferred alkaline catalyst.

The amount of alkaline catalyst applied will, of course, vary with the particular catalyst, with the chain bulking agent and to some extent with the amount of water present in the fabric. Ordinarily it will range from 1 to 9% by weight of dry cellulose.

The chain bulking agent may be applied in any convenient way. The method chosen will normally depend on the characteristics of the particular reactant. If the reactant is a liquid it can be applied as such. If it is a liquid or a solid it can be applied as an aqueous solution or dispersion or as a solution in a suitable organic solvent such as benzene. The proportion will depend to a great measure on the precise agent being used. Usually, however, it will be between 6 and 30% on the weight of dry cellulose.

In carrying out the treatment it is normally preferred to first saturate the fabric with an aqueous solution of the alkaline catalyst. In this process the fabric will also normally pick up the desired quantity of water.

Following impregnation of the fabric with alkaline catalyst, the reactant itself is applied.

After impregnation with chain bulking agent and alkaline catalyst the fabric is cured. Hitherto it had been considered necessary to store the impregnated fabric in an air tight container for an extended time, often a matter of hours, to secure proper reaction. In accordance with a particular feature of the present invention, however, the reaction is carried out at elevated temperature and pressure and under these conditions may be completed in a matter of a few minutes or even a few seconds. Thus, for example, if the impregnated material is sealed in a pressure vessel and exposed to a temperature above 100°C., preferably 110°—150°C., under autogeneous pressure, normally of the order of 5 to 120 pounds/sq. inch gauge, it is found that a

large proportion of the material is reacted within 5 seconds to 15 minutes.

In the laboratory these observations can be confirmed using an autoclave; on a commercial scale the Montforts reactor can be employed. (See American Dyestuff Reporter 49, pp. 351—353, 362).

It should be understood that it is not essential that the alkaline catalyst be applied first; if desired the fabric can first be coated with the chain bulking agent and the water and catalyst added subsequently. However, in this case, care must be taken that the reactant is not leached out of the fabric during the application of the catalyst, as, for example, by using applicator rolls.

In certain cases the chain bulking reagent and the alkaline catalyst may be applied from a single aqueous solution. However, in general, this is not desirable since the alkali will in many cases cause hydrolysis of the reagent.

Following treatment with the chain bulking agent as described above, the fabric will have a wet crease recovery angle between about 30° and about 60° higher than after the dry cross linking treatment and higher still compared with untreated fabric. Its dry crease recovery may be somewhat lower than was the case following the dry treatment. This, however, can be controlled by controlling the conditions of reaction; for example, potassium hydroxide has far less effect on the formaldehyde bonds than, for example, sodium hydroxide.

It will be observed that, in the foregoing description, the formaldehyde cross-linking reaction is described as preceding the chain bulking reaction. This is the preferred sequence of treatments, and indeed with the preferred chain bulking agent, epichlorohydrin, little cross-linking is obtained if the epichlorohydrin is applied first. On the other hand, with other chain bulking agents, for example with 1,3-dichloro-2-propanol, better results are obtained when the chain bulking reagent is applied before the formaldehyde.

The reactions which occur during the chain bulking reaction may vary considerably depending on the reagent used. With certain reagents additional cross-linking may occur. However, as noted above, cross-linking is not necessary for raising the wet crease recovery angle, and it is considered that with the preferred reagent, epichlorohydrin, cross-linking does not occur.

In any case, it is found that by the combined use of a dry cross-linking reaction using formaldehyde as the cross-linking agent, and reaction of the cellulose while in the swollen state with a bulking reagent having at least 3 carbon atoms, high wet and dry crease recovery angles can both be obtained.

The invention will be further described by reference to the following specific examples.

EXAMPLE 1

Four samples, labelled A, B, C and D, of a white cotton shirting fabric having 91 ends per inch and 92 picks per inch are treated in the following manner:

Samples A and B are soaked for five minutes in a solution having a pH of 7 and containing, by weight, 1% HCHO and 2% MgCl₂·6H₂O, padded to 100% pickup, framed to size, dried at 80°C. for ten minutes and cured at 150°C. for five minutes. They are then washed and pressed dry.

Sample A is not further treated.

Sample B and Sample C are then soaked for three minutes in 3% aqueous KOH, padded to 100% pickup, dipped in epichlorohydrin, allowed to drain to approximately 10% pickup of epichlorohydrin, heated for 1 minute at about 140°C. in a closed container, washed and dried.

Sample D is a control and is not treated at all.

The samples are then analysed, where appropriate, for bound formaldehyde and then their water inhibition and crease recovery angles, wet and dry, are determined. The results are tabulated in Table I.

TABLE I

Sample	% Bound HCHO	WI ¹ %	CRA ²	
			Dry	Wet
A	0.26	32	210	233
B	0.32	28	238	286
C	—	43	150	230
D	—	—	144	189

¹) "WI%" means water imbibition. "Water imbibition" as used in this specification means the *percent* by weight of water retained in saturated material after centrifuging a 0.5 g. sample for 5 minutes at 1000G. It is expressed as *percent* of the oven dry weight of the cellulose.

²) "CRA" means "crease recovery angle" (see the second paragraph of this specification). The values given are in degrees and represent the sum of the angles measured in the direction of warp and weft.

A study of these results indicates that the combined treatment in accordance with the invention gives better crease recovery angles, both wet and dry, than could be anticipated from the results of either treatment taken alone.

EXAMPLE 2

The same material as is used in Example 1 is treated with an aqueous solution having a pH of 7 and containing, by weight, 2% HCHO and 3% MgCl₂·6H₂O, padded to 100% pickup, dried and cured as in Example 1. It is then soaked for three minutes in 3% aqueous KOH, padded to 100% pickup, dipped in epichlorohydrin, drained to about 10% pickup, stored overnight in a polyethylene bag, washed and dried. The fabric contains 0.45% bound HCHO, and has a water imbibition of 28%. Its cross recovery angles are (dry) 243° and (wet) 286°.

EXAMPLE 3

A sample of the fabric used in Examples 1 and 2 is treated as in Example 2 with a 2% HCHO—3% MgCl₂·6H₂O solution, dried, cured, washed and dried. It is then soaked for 3 minutes in 3% aqueous KOH, dipped in 1,3-dichloro-2-propanol, drained to about 10% pickup, and stored overnight in a polyethylene bag. After washing and drying the sample is found to contain 0.62% bound HCHO. It has a water imbibition of 29%, a dry crease recovery angle of 225° and a wet crease recovery angle of 229°.

EXAMPLE 4

The procedure of Example 1 (Sample 8) is repeated *except* that the order of treatment is reversed, i.e. the material is first treated with 3% KOH and epichlorohydrin and subsequently treated with a 1% HCHO—2% MgCl₂·6H₂O solution. Only a trace of formaldehyde is found in the product, which has a water imbibition of 42%, a dry crease recovery angle of 170° and a wet crease recovery angle of 209°.

EXAMPLE 5

The procedure of Example 3 is repeated *except* that the order of treatment is reversed, i.e. the fabric is first treated with 1,3-dichloro-2-propanol and 3% aqueous KOH as described in Example 3 and then with 2% HCHO and 3% MgCl₂·6H₂O, also as in Example 3. The product contains 0.34% bound HCHO, has a water imbibition of 29%, a dry crease recovery angle of 237° and a wet crease recovery angle of 228°.

EXAMPLE 6

Four samples of a viscose rayon gabardine having 140 ends per inch and 59 picks per inch, labelled E, F, G and H, are treated as follows:

Samples E and F are soaked for five minutes in an aqueous solution having a pH of 6 containing (wt %) 4% HCHO and 5% MgCl₂·6H₂O. After padding to 100% pickup, they are framed to dimension, dried at 80°C. for 10 minutes and cured for five

minutes at 150°C. They are then washed and pressed dry.

Sample E receives no further treatment.

Sample F and Sample G are soaked for 3 minutes in 3% aqueous KOH, padded to 100% pickup, dipped in epichlorohydrin, drained to about 10% pickup, and heated in a closed vessel for 1 minute at a temperature of about 140°C. Pressure in the

vessel reaches about 50 psig. Following this, they are washed and dried.

Sample H is a control sample and is not treated at all.

Following the above procedure, the samples are tested for bound formaldehyde content, where appropriate, water imbibition and dry and wet crease recovery. The results are tabulated in Table II.

TABLE II

Sample	Bound HCHO	WI%	CRA	
			Dry	Wet
E	0.57	49	194	201
F	0.65	50	209	261
G	—	77	194	242
H	—	—	184	137

Again the effect of the combined treatment (Sample F) is greater than could have been predicted from the individual treatments E and G.

EXAMPLE 7

Another sample of the same fabric used in Example 6 is treated with an aqueous solution (pH 6) containing 4% HCHO and 5% $MgCl_2 \cdot 6H_2O$, dried and cured as described in Example 6. It is then soaked for three minutes in 3% aqueous KOH, padded to 100% pickup, dipped in 1,3-dichloro-2-propanol, drained to 10% pickup, placed in a polyethylene bag and stored for 12 hours. Following this it is washed and dried. The finished fabric contains 1.2% bound HCHO. It has a water imbibition of 41%, a dry crease recovery angle of 205° and a wet crease recovery angle of 200°. The same fabric treated with the dichloropropanol alone, i.e. without a prior formaldehyde treatment, has a water imbibition of 79%, a dry crease recovery angle of 183%, and a wet crease recovery angle of 184°.

EXAMPLE 8

The order of treatment in Example 6 (Sample F) is reversed. Thus the same fabric is soaked in 3% aqueous KOH, padded to 100% pickup, dipped in epichlorohydrin, drained to 10% pickup, heated to 130°C. for 1 minute in a closed container, washed, dried, impregnated with a solution of 4% HCHO and 5% $MgCl_2 \cdot 6H_2O$ at pH 6, padded to 100%, dried and cured as in Example 6. The product contains 0.11% bound HCHO. It has a water imbibition of 70%, a dry

crease recovery angle of 209° and a wet crease recovery angle of 242°.

EXAMPLE 9

Example 7 is repeated, again reversing the order of treatment. Thus another sample of the same rayon gabardine is treated first with KOH and 1,3-dichloro-2-propanol and then with HCHO and $MgCl_2 \cdot 6H_2O$ using the same reaction conditions used in Example 7. The product contains 1.3% HCHO. It has a water imbibition of 38%, a dry crease recovery angle of 251° and a wet crease recovery angle of 235°.

EXAMPLE 10

To compare the effect of applying the chain bulking agent in a solution of an inert organic solvent and in an aqueous KOH slurry the following experiments are performed.

Samples of a cotton broadcloth fabric are treated as follows:

Sample J is soaked in a slurry containing 3% KOH and 8% epichlorohydrin for 5 minutes, padded to 90% pickup and stored overnight in a polyethylene bag.

Samples K, L and M are soaked in 3% aqueous KOH for 3 minutes, padded to 100% pickup, dipped in solution of epichlorohydrin and toluene containing 25%, 50% and 75% by weight epichlorohydrin, respectively, drained to 10% pickup and stored in polyethylene bags overnight.

Sample N is treated as samples K, L, and M but with pure epichlorohydrin.

Sample O, a control sample, is not treated.

The samples are washed, dried and tested for wet and dry crease recovery angle. The results are given in Table III below.

TABLE III

Sample	Treating Agent	CRA	
		Dry	Wet
J	8% epichlorohydrin slurry	202	264
K	25% epichlorohydrin	213	269
L	50% „	216	288
M	75% „	208	271
N	100% „	222	304
O	control	193	217

These experiments indicate that while aqueous dispersions and organic solutions of the chain bulking agent may be used, it is generally more effective to use the pure reagent wherever practicable.

WHAT WE CLAIM IS:—

1. A method for improving the properties of cellulosic textile material, comprising cross-linking the cellulose with formaldehyde while the cellulose is substantially dry as hereinbefore defined and reacting the cellulose in a swollen state with a chain bulking agent, as hereinbefore defined, either before or after the cross-linking.

2. A method as claimed in claim 1, in which the cross-linking is carried out by impregnating the material with formaldehyde, water and a catalyst for the cross-linking, which catalyst is zinc sulphate or a melt of a bivalent group II metal with a monobasic acid, which is at least 50 per cent ionized in normal aqueous solution at 18°C, and then drying and heating the impregnated material.

3. A method as claimed in claim 1 or claim 2, in which the catalyst is one which is soluble to the extent of at least 0.03 mols/litre in water at 20°C. and pH5.

4. A method as claimed in claim 3, in which the catalyst is a magnesium halide.

5. A method as claimed in claim 4, in which the catalyst is magnesium chloride.

6. A method as claimed in any of claims 1 to 5, in which the material is impregnated with at least 0.003 g.-mols of the catalyst for the cross-linking per 100 grams of cellulose.

7. A method as claimed in any of claims 1 to 6, in which the reaction with a chain bulking agent is carried out in the presence of liquid water at a temperature in the range of 110° to 150°C.

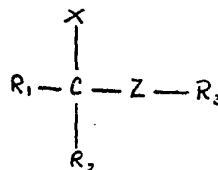
8. A method as claimed in any of claims

1 to 7, in which the reaction with a chain bulking agent is carried out in the presence of an alkaline catalyst for the reaction.

9. A method as claimed in claim 8, in which the alkaline catalyst is sodium hydroxide or potassium hydroxide.

10. A method as claimed in any of claims 1 to 9, in which the chain bulking agent is an organic compound having at least three carbon atoms and at least one functional group capable of reacting with cellulose.

11. A method as claimed in claim 10, in which the chain bulking agent is one having the general formula:—



or $\text{R}_1 - \text{Z} - \text{Z} - \text{R}_3$
or $\text{R}_1 - \text{Z} - \text{R}_4 - \text{Z} - \text{R}_3$

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in which R_1 , R_2 , R_3 , R_4 , X and Z have the meanings hereinbefore ascribed to them.

12. A method as claimed in claim 11, in which the chain bulking agent is epichlorohydrin and the reaction with epichlorohydrin is carried out after the cross-linking.

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13. A method as claimed in claim 11, in which the chain bulking agent is a dichloropropanol.

14. A method as claimed in claim 13, in which the chain bulking agent is 1,3-dichloro-2-propanol.

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15. A method for improving the properties of cellulosic textile material, as claimed in any of claims 1 to 14 and substantially as

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hereinbefore described and illustrated by way of the Examples 1—9.

- 5 16. Cellulosic textile material, including fibres and fabrics, which have been subjected to treatment by a method as claimed in any of the preceding claims.

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